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Removal of Thiosulphate Ion from Aqueous Stream using H_2O_2 Advanced Oxidation Process with UV Light

by

Suqainah Binti Khairus

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

OCTOBER 2009

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CERTIFICATION OF APPROVAL

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TRONOH, PERAK

October 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SUQAINAH BINTI KHAIRUS

ABSTRACT

This report basically discusses the research done, experimental data and the development of kinetic model. A few experiments are conducted by varying few parameters which are Thiosulphate concentration (400ppm to 1200ppm), Hydrogen Peroxide concentration (0.1M to 0.5M) and UV light power supply (4W to 12W). The temperature and pH value is recorded as well as the formation of sulfate. Last but not least, a kinetic model is developed using the experimental data collected

ACKNOWLEDGEMENTS

First and foremost, I would like to praise my Lord God for His grace and mercy throughout the progress of my Final Year Project. I also would like to acknowledge both my parents and also my family for always being supportive to provide financial and moral support.

I would also like to take this special opportunity to honourably thank to my Final Year Project supervisor, Dr. Farooq Ahmad, for spending in personal time to further educate and assist me on the project undertaken while endlessly contributing reading materials which helped me a lot as my reference. He also taught me the aspects needed to complete my Final Year Project and the methodology to be used to analyze the project so that the needed result can be obtained.

I would also like to express my special thanks to all lecturers and others who have either directly or indirectly contributed to the project by giving priceless information on how to conduct and improve the project. Without such assistance from these people, this Final Year Project might not be as successful as it is.

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CHAPTER 1

INTRODUCTION

1. BACKGROUND

Thiosulfate ($S_2O_3^{2-}$) is an oxyanion of sulfur produced by the reaction of sulfite ions with elemental sulfur in boiling water,

$$S(s) + SO_3^{2-}(aq) \rightarrow S_2O_3^{-2}(aq)$$

that occurs naturally in hot springs and geysers, and is produced by certain biochemical processes. In the body, thiosulfate converts small amounts of cyanide ion into harmless products and plays a role in the biosynthesis of cysteine, a sulfur-containing amino acid that locks proteins into their correct three-dimensional shapes. It is not found in large quantities in nature. Solutions of thiosulfate break down into sulfur, sulfites, and sulfates when exposed to acids, light, metal ions, and bacteria.

It acts as a reducing agent. It is routinely used as a titrant to determine concentrations of oxidants such as hypochlorite in bleach and dissolved oxygen in water. It instantly dechlorinates water, and is used to stop bleaching action in the paper-making industry. Thiosulfate forms water-soluble complexes with many metals, making it useful in photoprocessing (where it dissolves excess silver bromide on the surface of exposed film, preventing excessive darkening). Thiosulfate is also useful in the extraction of silver from silver ore, in leather manufacture, and as a mordant in the textile industry.

2. PROBLEM STATEMENT

The sulfur in the gaseous fuels is predominantly present in the form of H_2S, SO_2, and organic sulfur compounds. During the processing of the natural gas obtained from offshore gas production installations, the sulfur present in the natural gas is oxidized through a caustic oxidation process, and the wastewater generated contains predominantly thiosulfate at a concentration as high as 3000 mg/L (permissible limit is 100 mg/dm^3). This wastewater is normally referred to as caustic spent wash, and this wastewater causes severe pollution problems if discharged without treatment. (*Khanna et al,1996*)

Thiosulfate ion ($S_2O_3^{2-}$) is used in a variety of industrial process such as in natural gas processing, paper and mining industry and it likely to become part of industrial waste water stream. Since a number of microorganisms using thiosulfate ion as an energy source whereby thiosulfate ion is oxidize and oxygen consumed, this contributes to high biochemical oxygen demand (BOD) and lowering the pH due to formation of sulphuric acid during oxidation process and will potentially impact the resident biotic community (*Schreiber et al,1997*).

Different processes for the oxidation of thiosulfates have been proposed. Takizawa et al. (1973), studied the reaction of thiosulfates with ozone solution in the range 10–80 °C, resulting in a mixture of sulfate, trithionate and tetrathionate. Chanda and Rempel (1986), studied the oxidation of thiosulfates and tetrathionate to sulfate, using air, catalyzed by Cu_2O, at 50–70 °C. Xu et al. (1996), proposed the oxidation of thiosulfates by oxygen, using synthetic sphalerite doped with transition metals. Sato et al. (2003), proposed an oxidation reaction of thiosulfates by hydrogen peroxide at −15 °C, obtaining tetrathionate as an intermediate product and finally sulfates *(Gonzalez-Lara et al, 2008)*. Based on Eckenfelder (1997), hydrogen peroxide AOP with the combination of UV light have been successfully implemented as treatment system for variety of industrial waste water. This paper will present whether this technique applicable and effective for thiosulfate removal as compared to other oxidation process.

3. OBJECTIVE AND SCOPE OF STUDY

3.1. Objective

i) To apply a technique of thiosulfate oxidation using H_2O_2 advance oxidation with UV light.

ii) To determine the parameters which affect the H_2O_2 advance oxidation (concentration of H_2O_2 and thiosulfate, UV power)

iii) To develop kinetic models representing the H_2O_2 advance oxidation process.

3.2. Scope of Study

The scope of work for the first stage of the project is focusing on research and literature review while for second stage is focusing on lab experiment kinetic model development. The lab experiment would be conducted by varying few parameters such as thiosulfate concentration, hydrogen peroxide concentration and power supply for UV light.

CHAPTER 2

LITERATURE REVIEW AND THEORY

1. LITERATURE REVIEW

In this section, background information on research project will be discussed to give better understanding on the project.

1.1. Thiosulfate

For this final year project, thiosulfate is the substance that wants to be removed from the waste water by using proposed method.

1.1.1. Structure of thiosulfate ion

Structurally, thiosulfate is similar to sulfate. The molecule has a slightly distorted tetrahedral shape with a central and a peripheral sulfur ($S\text{-}SO_3$). Sulfur is larger than oxygen and forms weaker πbonds, so the S-S bond is somewhat longer than the S-O bonds (1.99 +/- 0.03 A vs. 1.48 +/- 0.06 A, respectively) (*Nardelli and Fava, 1962)*

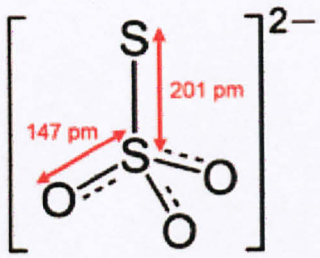


Figure 2.1: Structure of thiosulfate ion

1.1.2. Source of thiosulfate ion

Thiosulfate is not found in large quantities in nature , it is mostly produce by several reactions

i) Reaction of sulfur with sodium sulfite in boiling aqueous solution,

$$S_8 + 8\ SO_3^{2-} \rightarrow 8\ S_2O_3^{2-}$$

ii) Reaction of SO_2 gas with sulfide/carbonate liquor (a byproduct of paper manufacturing).

iii) As a byproduct in the manufacture of sulfur dyes.

1.1.3. Thiosulfate application

i) *Photographic fixing agent*. An emulsion of sodium thiosulfate (called *hypo* by photographers) is used to stop development of exposed film. Thiosulfate converts undeveloped silver bromide grains in the film into water-soluble silver thiosulfate complexes that can be removed when the film is washed.

$$S_2O_3^{2-} + AgBr(s) \rightarrow AgS_2O_3^{-} + Br^{-}$$
$$S_2O_3^{2-} + AgS_2O_3^{-} \rightleftharpoons Ag(S_2O_3)^{3-}$$

ii) *Extracting silver from ores*. Thiosulfate's ability to convert silver compounds into soluble silver complexes also makes it useful in ore processing.

iii) *Paper manufacture and dechlorination of water*. Thiosulfate ion is used to remove chlorine (hypochlorite) from water or from solutions used to bleach paper pulp:

$$HOCl + 2\ S_2O_3^{2-} \rightarrow Cl^{-} + S_4O_6^{2-} + OH^{-}$$

iv) *Dissolved oxygen testing and chemical analysis of oxidants.* Thiosulfate is a reducing titrant used for determining many oxidizing agents. For example, hypochlorite concentrations in bleach can be determined using the reaction above. Thiosulfate is also used as a titrant in determining BOD.

v) *Whitening cotton fabrics, bone, straw, and ivory.* Some materials are weakened or yellowed when bleached. Thiosulfate solutions can sometimes be used to whiten these materials.

1.1.4. Thiosulfate affects on environment

i) Thiosulfate is an antidote for cyanide poisoning. It reacts with cyanide to produce sulfite and thiocyanate ions:

$$CN^- + S_2O_3^{2-} \rightarrow SCN^- + SO_3^{2-}$$

This reaction is catalyzed by an enzyme produced by cell mitochondria to neutralize small quantities of ingested cyanide (which occurs naturally in cassava root, lima beans, and almonds).

ii) Thiosulfate is an intermediate in several biochemical pathways, including the synthesis of L-cysteine (an amino acid). Thiosulfate is manufactured by some cells by oxidation of elemental sulfur and by degradation of L-cysteine.

iii) Thiosulfate breaks down rapidly in the environment due to the action of air and certain bacteria, eventually producing sulfides and sulfates.

1.2. Advanced Oxidation Process (AOP)

The need for "clean" treatment technologies, e.g., techniques which do not result in the creation of either more hazardous or environmentally damaging by-products or more concentrated waste streams, has led to increased interest in advanced oxidation processes (AOPs). AOPs are defined as near ambient temperature and pressure water treatment processes, based on the in situ generation of radicals (particularly hydrogen radicals HO) to initiate oxidative destruction of organic and inorganic contaminants (Vogelpohl and Kim, 2004).

AOPs which involve the *in situ* generation of highly potent chemical oxidants such as the hydroxyl radical (OH•), have emerged as an important class of technologies for accelerating the oxidation and hence destruction of a wide range of organic contaminants in pollution solids, water and air(C.W. Jones, 1999)The majority of AOPs utilize hydrogen peroxide as a source of hydroxyl radicals (OH•). These OH• radicals constitute a very powerful, non-selective oxidant, which reacts much faster than either atomic oxygen or ozone. These radicals are highly reactive short-lived species that will attack and destroy many organic substances present in the aqueous solution. The hydroxyl radicals were generated using a combination of ozone and UV utilizing commercially available equipment. Ozone has a strong UV absorbance at around 254 nm and decomposes rapidly in water to give hydrogen peroxide and then hydroxyl radicals. The oxidation potential of HO• is 2.80 V as opposed to 2.42 V of atomic oxygen and 2.07 V of ozone. This greater oxidizing potential has the effect of reducing the time of the reaction thus reducing the system size and the cost of treatment (Legrini et al., 1993).

The most common AOP are:

i) Fenton's treatment
ii) UV/H_2O_2
iii) O_3/ H_2O_2
iv) $UV/O_3/ H_2O_2$ combinations

Hydroxyl radicals are produce from hydrogen peroxide via different pathways and to different efficiencies depending on the nature of the catalyst (AOP system) involved. Figure 3 demonstrates hydroxyl radical production efficiencies for the three most commonly applied technologies: Fenton's treatment, UV/H_2O_2, O_3/ H_2O_2.

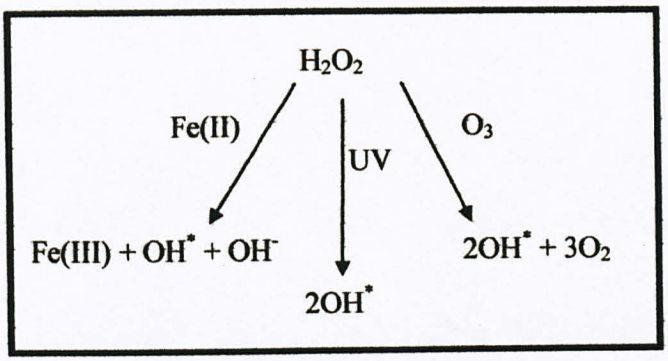


Figure 2.2: hydroxyl radical production

Whilst all of the above systems are capable of breaking down biorecalcitrant species to innocuous product, the best system for a particular application will be dependent upon several factors including:

i) Nature of the polluted medium (solid, aqueous or gaseous)
ii) Total load of oxidizable species
iii) Existing and target pollutant levels
iv) Availability of secondary treatment or pre-treatments, *e.g.* biotreatment
v) Effluent characteristic, including flow rate, flow regularity, temperature and pH
vi) Discharge constraints.

1.3. Hydrogen Peroxide

Hydrogen peroxide has been used to reduce the BOD and COD of industrial wastewaters for many years. While the cost of removing BOD/COD through chemical oxidation is typically greater than tat through physical or biological means, there are nonetheless specific situations which justify its use. These include:

i) Predigestion of wastewaters which contain moderate to high levels of compounds that are toxic, inhibitory, or recalcitrant to biological treatment (e.g., pesticides, plasticizers, resins, coolants, and dyestuffs);

ii) Pretreatment of high strength / low flow wastewaters – where biotreatment may not be practical – prior to discharge to a Publicly Owned Treatment Works (POTW);

iii) Enhanced separation of entrained organics by flotation and settling processes; and

iv) Supply of supplemental Dissolved Oxygen (DO) when biological treatment systems experience temporary overloads or equipment failure.

As indicated by these examples, H_2O_2 can be used as a stand-alone treatment or as an enhancement to existing physical or biological treatment processes, depending on the situation.

H_2O_2 can be used alone or with catalysts – such as iron (Fe2+ or Fe3+), UV light, ozone (O_3) and alkali – to oxidize BOD/COD contributing compounds in wastewaters. The type of oxidation needed depends on the type of BOD/COD present. This relationship is present in the Table 2.1 below.

Table 2.1: Oxidant system for few types of pollutants.

Oxidant System	Chemical Oxygen Demand Type A (Sulfide, Thiosulfate, Sulfite)	Type B (Phenols, Cyanides, Amines)	Type C (BTEX, TOCl, Paraffins)
Type A			
H_2O_2	X		
Type B			
H_2O_2 / OH-	X	X	
H_2O_2/ M+	X	X	
H_2O_2 / H+	X	X	
Type C			
H_2O_2 / Fe	X	X	X
H_2O_2 / O_3	X	X	X
H_2O_2 / UV	X	X	X

Note: Whether an oxidant system will degrade a specific pollutant (i.e., affect its COD) will depend on the oxidant system and the pollutant. Type A oxidants react only with Type A pollutants; whereas, Type C oxidants, being more reactive, react with most any pollutant. However, Type C oxidants generally react preferentially with Type A pollutants.

1.4. Ultraviolet (UV) light

Ultraviolet (UV) light is electromagnetic radiation with a wavelength shorter than that of visible light, but longer than x-rays, in the range 10 nm to 400 nm, and energies from 3 eV to 124 eV. It is so named because the spectrum consists of electromagnetic waves with frequencies higher than those that humans identify as the color violet.

UV light is found in sunlight and is emitted by electric arcs and specialized lights such as black lights. As an ionizing radiation it can cause chemical reactions, and causes many substances to glow or fluoresce. Most people are aware of the effects of UV through the painful condition of sunburn, but the UV spectrum has many other effects, both beneficial and damaging, on human health.

1.4.1. Ultraviolet waves

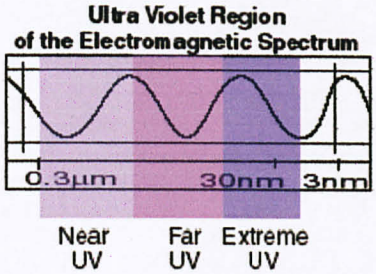


Figure 2.3: UV region

Scientists have divided the ultraviolet part of the spectrum into three regions: the near ultraviolet, the far ultraviolet, and the extreme ultraviolet. The three regions are distinguished by how energetic the ultraviolet radiation is, and by the "wavelength" of the ultraviolet light, which is related to energy.

The near ultraviolet, abbreviated NUV is the light closest to optical or visible light. The extreme ultraviolet, abbreviated EUV, is the ultraviolet light closest to X-rays, and is the most energetic of the three types. The far ultraviolet, abbreviated FUV, lies between the near and extreme ultraviolet regions. It is the least explored of the three regions.

1.4.2. Subtypes of UV light

The electromagnetic spectrum of ultraviolet light can be subdivided in a number of ways. The draft ISO standard on determining solar irradiances (ISO-DIS-21348) describes the following ranges:

Table 2.2: subtypes of UV light

Name	Abbreviation	Wavelength range in nanometers	Energy per photon
Ultraviolet A, long wave, or black light	UVA	400 nm–320 nm	3.10–3.94 eV
Near	NUV	400 nm–300 nm	3.10–4.13 eV
Ultraviolet B or medium wave	UVB	320 nm–280 nm	3.94–4.43 eV
Middle	MUV	300 nm–200 nm	4.13–6.20 eV
Ultraviolet C, short wave, or germicidal	UVC	280 nm–100 nm	4.43–12.4 eV
Far	FUV	200 nm–122 nm	6.20–10.2 eV
Vacuum	VUV	200 nm–10 nm	6.20–124 eV
Extreme	EUV	121 nm–10 nm	10.2–124 eV

In sunlight, UV radiations, is classified into three types by its wavelength: UVA ranges from 400 to 320 nm, UVB from 320 to 290 nm, and UVC from 290 to 200 nm. The shorter the wavelength, the more harmful the energy it carries. Our earth is surrounded by a defensive shield of gases which absorbs all of the UVC radiation and some of the UVA and UVB radiation.

UV light in AOP and wastewater treatment

Bacteria, viruses, and other micro organisms are sensitive to UV light at a particular wavelength at 253.7 nanometers. Their reproductive capability is destroyed by cross linking and splitting their DNA, which means that they are inactivated and no longer constitute a threat to human health.

In the ultraviolet disinfection system the water is passing in submerged UV lamps emitting lethal doses of energy, destroying the pathogens. Its strength depends on the UV light intensity and the time of exposure.

Disinfection is achieved with ultraviolet (UV) light in combination with an advanced oxidation process (AOP) mediated by the addition of hydrogen peroxide (H_2O_2). The use of UV and AOP mitigates the use of chlorine, which is known to contribute to the formation of disinfection byproducts (DBPs). The UV light provides disinfection against bacteria and viruses and directly photolyzes nitrosodimethylamine (NDMA), a suspected carcinogen. AOP is achieved when UV light reacts with H_2O_2 to form highly reactive hydroxyl radicals (•OH), which oxidize organic components in the feedwater. The inclusion of AOP with H_2O_2 provides an additional layer of disinfection and treatment of contaminants that are not directly photolyzed by UV light.

CHAPTER 3

METHODOLOGY

1. RESEARCH METHODOLOGY

Few researches on the topic and collecting information from various source i.e internet, journals and books is done to have better understanding on thiosulfate removal, hydrogen peroxide, advanced oxidation and the effect of UV light presence for wastewater treatment.

2. PROJECT ACTIVITIES

2.1. Lab experiment for parameters testing

The experiment will be conducted in UTP chemical laboratory. A few parameters that affect the thiosulfate removal will be monitored to determine the optimum parameter and condition to give maximum rate of thiosulfate removal. These parameters will be used to analyze thiosulfate's concentration drop and developing the kinetic model

Table 3.1: Variables for lab experiments

Experiment	Manipulated Variable	Constant Variable
1	- Thiosulfate ions concentration ($S_2O_3^{2-}$ concentration) [400 – 1200ppm]	-Ultraviolet light (4W) -H_2O_2 concentration (0.1M)
2	-H_2O_2 concentration [0.1 – 0.5 mol]	-Ultraviolet light (4W) -Thiosulfate concentration (600ppm)
3	-Ultraviolet light power supply [4, 8, 112 W]	-Thiosulfate concentration (600ppm) -H_2O_2 concentration (0.1M)

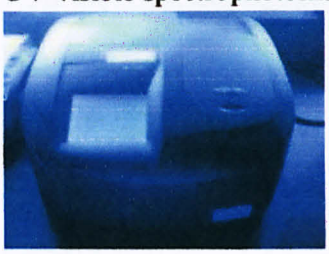
2.1.1. Chemical used

Table 3.2: Chemical used

Chemical	Purpose
Sodium sulfate	- Used to develop standard curve for UV-vis spectrophotometer
Sodium thiosulfate	- Main solution used - Will be react with H_2O_2 in range of 400 -1200ppm
sulfaVer 4 reagent	- Use for uv-vis to indicate the sulphate formation in the sample
Hydrogen peroxide	- Use as oxidizing agent and will react with thiosulfate solution in range of 0.1 – 0.5M

2.1.2. Equipment used

Table 3.3: Equipment used

Equipment	Purpose
Glass reactor (1.5 L beaker)	Used as mixing container for thiosulfate and H_2O_2 reaction
UV-visible spectrophotometer  Figure 1 : UV-vis spectrophotometer	A device to measure light intensity as a function of the wavelength of light. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I / I_o are called the *transmittance*, and are usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance: $A = -\log(\%T / 100\%)$
UV bulb	To supply UV light to the solution
pH probe	To measure the pH of the solution
Thermometer	To measure the temperature of the solution

2.2. Procedure

2.2.1. Develop standard curve for UV-vis spectrophotometer

Prepare 7 standard sulfate solutions (10ppm-70ppm)

1) Dissolve 1 gram of sodium sulfate in 1 Liter of distilled water using 1 Liter volumetric flask.
2) Mark it as 1000ppm standard solution
3) Next, prepare 7 solutions from standard solution with concentration of 10,20,30,40,50,60 and 70 ppm
4) Solution from each concentration will be measured using UV-vis spectrophotometer.

Test on the UV-vis spectrophotometer

1) Select the "sulfate" test on the UV-vis spectrophotometer.
2) Insert the Multi-cell Adapter with the 1-inch square cell holder facing the user
3) Fill a square sample cell with 10 ml of 10 ppm solution
4) Add the content of one SulfaVer 4 Reagent Powder Pillow to the sample cell. Swirl vigorously to dissolve powder. (prepared sample)
5) Press TIMER>OK. A 5 minutes reaction period will begin

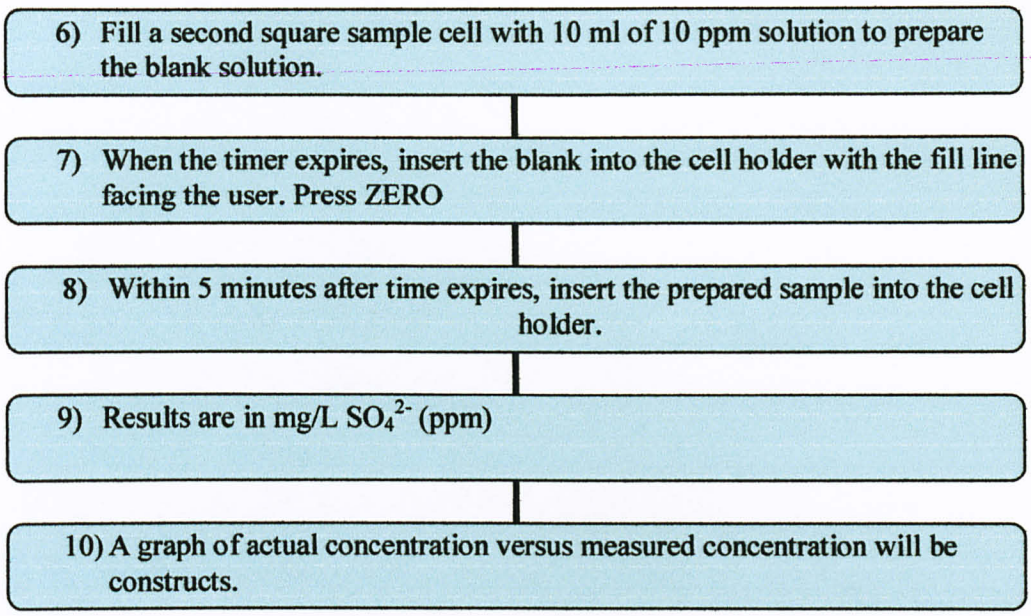


Figure 3.1: Process flow for standard curve development

2.2.2. Experiment 1, 2 and 3

These three experiments will be conducted in a batch reactor. Hydrogen Peroxide advance oxidation of thiosulfate ion has been done by adding certain concentration of hydrogen peroxide to the batch reactor. Samples are withdrawn from time to time and analyzed by UV visible spectrophotometer instead of chromatographic technique and old titration technique. The effects of concentration of thiosulfate ion, concentration of hydrogen peroxide, and UV light presence will be investigated.

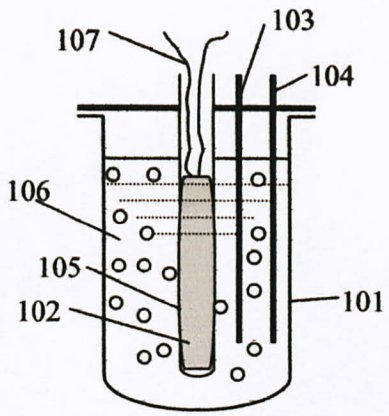


Figure 3.2: Experimental setup

Referring FIG. 5, there is shown an experimental setup to demonstrate the process of removing thiosulfate ions from a solution, comprising a glass reactor (101), a UV emitting lamp (102), a pH probe (103), and a thermometer (104). The UV emitting lamp (102) is connected to power supply (107). This experiment is used to emulate the actual implementation of the same process on wastewater, whereby oxidation of thiosulfate in wastewater (106) to generally harmless sodium sulphate occurs. It is to be noted that the pH probe (103) was dipped into the liquid (106) in the apparatus only to monitor the pH of the solution. On the basis of the experimental results given here we claim that we have invented a totally new method of thiosulfate oxidation in aqueous solution by exposure to UV radiation.

A glass reactor (101) is chosen to hold the liquid that is being tested, besides having a transparent body so that the activities in the glass reactor can be viewed and analyzed while keeping the UV lamp (102) off. The UV emitting lamp (102) used in the application is placed inside a tube made of quartz in order to transmit UV radiation from the source without absorption in the wall. This typed of arrangement is chosen in order to create the most efficient UV emission and absorption capability. Said quartz tube not only allows UV radiation to pass through effectively, but also protects the UV lamp (102) from the liquid when the UV lamp (102) and tube (105) is submerged into said liquid (106). Besides the UV lamp (102) and quartz tube (105), the thermometer (104) and pH probe (103) are also dipped into the liquid inside the glass reactor (101) in order to measure the temperature and pH of said liquid throughout the whole process.

3. PROJECT MILESTONE (GANTT CHART)

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Project Work Continue	■	■	■					Mid-Semester Break							
2	Submission of Progress Report 1				♦											
3	Project Work Continue				■	■	■	■								
4	Submission of Progress Report 2									♦						
5	Seminar (compulsory)										■	■	■			
5	Project work continue									■	■	■	■			
6	Poster Exhibition											♦				
7	Submission of Dissertation (soft bound)													♦		
8	Oral Presentation														♦	
9	Submission of Project Dissertation (Hard Bound)															♦

♦ Suggested milestone
■ Process

Figure 3.3: Gantt chart

CHAPTER 4

RESULTS AND DISCUSSION

1. EXPERIMENT 1

1.1. Objective

To study the effect of thiosulfate concentration to thiosulfate oxidation rate using UV/ H_2O_2 AOP

1.2. Variable

i) Hypothesis – As the concentration of thiosulfate increases, rate of thiosulfate oxidation increases

ii) Controlled variable – UV power, Hydrogen peroxide concentration

iii) Manipulated variable - thiosulfate concentration

1.3. Experiment Result

Table 4.1: Result for experiment 1

Time (min)		0	8	16	24	32	40	48
400 ppm	pH	3.33	2.67	2.38	2.35	2.29	2.25	1.98
	T (°C)	23	24	24	25	25	25	25.1
	mg/L	0	130	200	250	270	300	340
600 ppm	pH	6.41	6.05	5.15	2.96	2.56	2.52	2.48
	T(°C)	23.5	24	24	25	25	25	25.5
	mg/L	0	150	250	320	370	380	370
800 ppm	pH	5.66	5.57	5.48	3.38	2.88	2.55	2.43
	T(°C)	24	24.5	25	25	25.5	26	26.5
	mg/L	0	210	270	370	390	400	400
1000 ppm	pH	4.52	3.84	3.46	2.87	2.83	2.71	2.56
	T(°C)	23	23.2	24	25	25	25	25
	mg/L	0	240	310	390	410	420	460
1200 ppm	pH	4.75	4.55	4.3	3.72	3.23	2.9	2.81
	T(°C)	23	23	24	24	24	24.5	25
	mg/L	0	260	410	430	450	450	460

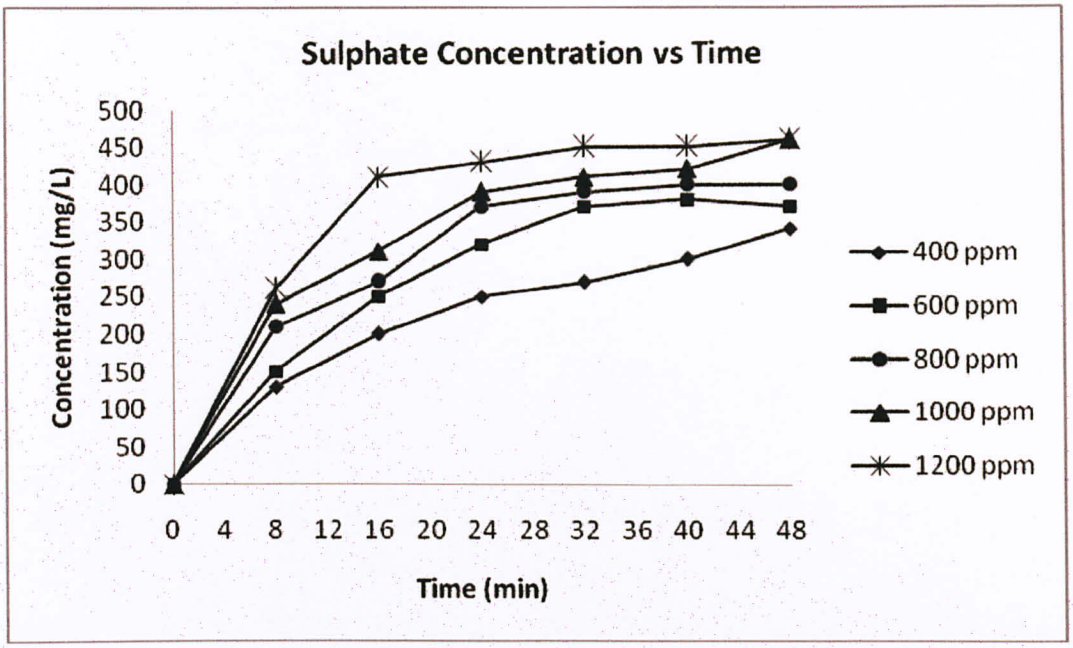


Figure 4.1: Graph of sulphate formation vs time (experiment 1)

1.4. Discussion

From the graph, it can be concluded that as the concentration of thiosulfate increases, the rate of sulphate formation increases. This is because more thiosulfate ions per volume react with hydrogen peroxide to produce sulphate. The result had proven the hypothesis made earlier.

2. EXPERIMENT 2

2.1. Objective

To study the effect of hydrogen peroxide concentration to the thiosulfate oxidation rate using UV/ H_2O_2 AOP

2.2. Variable

i) Hypothesis – As the concentration of hydrogen peroxide increases, rate of thiosulfate oxidation increases

ii) Controlled variable – UV power, thiosulfate concentration

iii) Manipulated variable – hydrogen peroxide concentration

2.3. Experiment Result

Table 4.2: Result for experiment 2

Time (min)		0	8	16	24	32	40	48
0.1M	pH	6.41	6.05	5.15	2.96	2.56	2.52	2.48
	T(°C)	23.5	24	24	25	25	25	25.5
	mg/L	0	150	200	230	270	300	300
0.2M	pH	5.85	3.28	2.8	2.6	2.44	2.38	2.31
	T(°C)	23	23.2	23.9	24	24.5	25	25
	mg/L	0	250	270	330	340	410	400
0.3M	pH	5.48	2.81	2.45	2.27	2.29	2.26	2.22
	T(°C)	30.5	30	30	30.5	30.5	31	30
	mg/L	0	150	210	260	300	290	290
0.4M	pH	4.8	2.61	2.46	2.32	2.29	2.26	2.23
	T(°C)	30	31	31	31	31	31	30.5
	mg/L	0	160	220	300	310	330	320
0.5M	pH	6.02	2.75	2.46	2.25	2.22	2.12	2.06
	T(°C)	24	24.5	25	25	25.5	26	26
	mg/L	0	120	150	210	190	210	240

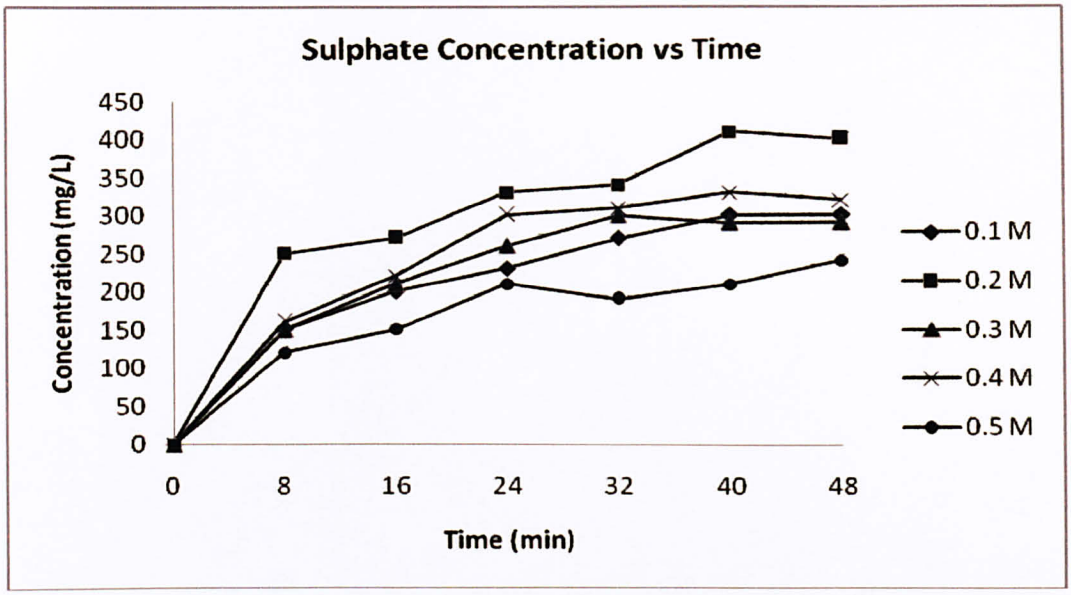


Figure 4.2: Graph of sulphate formation vs time (experiment 2)

2.4. Discussion

From the graph, the rate of sulphate formation increases from 0.1M to 0.2M. As the concentration is further increase from 0.3M to 0.5M, the rate of sulphate formation is lower as compared to 0.2M. Thus, the optimum concentration of hydrogen peroxide is 0.2M.

Amin et al (2008) stated this behavior is due to the fact that hydrogen peroxide is a scavenger for hydroxyl radicals according to the reaction given in the following equation (Buxton, 1988; Dionysiou et al., 2004):

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$$

$$2\ HO_2^{\bullet} \rightarrow H_2O_2 + O_2^{\bullet}$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$$

When enough hydrogen peroxide is present in the solution, it starts to compete with thiosulfate for reaction with hydroxyl radicals since $HO_2^{\bullet}$ is less reactive than the $OH^{\bullet}$ radical. An increased level of hydrogen peroxide has a diminishing effect on the reaction rate (Aleboyeh et al., 2005). In addition, the $OH^{\bullet}$ radicals generated at a high local concentration will readily dimerize to H_2O_2. Therefore, it is important to optimize the applied dose or concentration of hydrogen peroxide to maximize the performance of the UV/H_2O_2 process and minimize the treatment cost

3. EXPERIMENT 3

3.1. Objective

To study the effect of UV light to the thiosulfate oxidation rate using UV/ H_2O_2 AOP

3.2. Variable

i) Hypothesis – As the UV light power increases, rate of thiosulfate oxidation increases

ii) Controlled variable – Thiosulfate concentration, thiosulfate concentration

iii) Manipulated variable – UV light power

3.3. Experiment result

Table 4.3: Result for experiment 3

Time (min)		0	8	16	24	32	40	48
4 watt	pH	6.41	6.05	5.15	2.96	2.56	2.52	2.48
	T(°C)	23.5	24	24	25	25	25	25.5
	mg/L	0	130	200	230	260	290	300
8 watt	pH	6.41	6.05	5.15	2.96	2.56	2.52	2.48
	T(°C)	23.5	24	24	25	25	25	25.5
	mg/L	0	150	240	280	310	300	320
12 watt	pH	6.41	6.05	5.15	2.96	2.56	2.52	2.48
	T(°C)	23.5	24	24	25	25	25	25.5
	mg/L	0	190	330	310	320	300	290

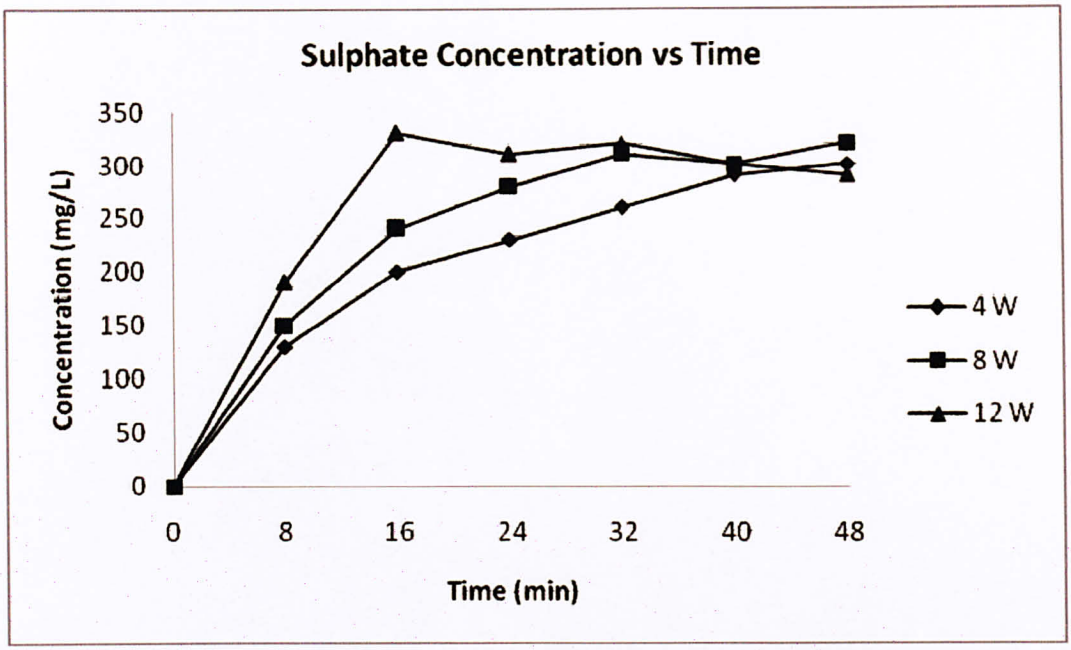


Figure 4.3: Graph of sulphate formation vs time (experiment 3)

3.4. Discussion

From the graph, it can be concluded that as the UV light power increases, sulphate formation rate increases. UV light plays two major roles in the reaction. First, it kills the microorganism and bacteria that use thiosulfate as their food that lead to high BOD condition. And second, it provides energy to hydrogen thiosulfate to produce more hydroxyl radical to react with thiosulfate.

Based on Amin et al (2008), exposure of a strong oxidizing agent to ultraviolet (UV) light generates hydroxyl free radicals, which are stronger than any other oxidants (Bolton and Cater, 1994). The hydroxyl radicals generated after activation have a higher oxidation potential (2.8 V) than hydrogen peroxide (1.78 V)

4. KINETIC MODEL DEVELOPMENT

The kinetic model is developed by using Integrated Rate Equation

The derivation of rate law:

$$r_1 \propto [H_2O_2]^{\alpha} \quad \ldots\ldots 1$$

$$r_2 \propto [S_2O_3^{2-}]^{\beta} \quad \ldots\ldots 2$$

$$r_1 = [H_2O_2]^{\alpha}$$

$$r_2 = [S_2O_3^{2-}]^{\beta}$$

$$\ln r = \ln k_1 + \alpha \ln [H_2O_2] \quad \ldots\ldots 3$$

$$\ln r = \ln k_2 + \alpha \ln [S_2O_3^{2-}] \quad \ldots\ldots 4$$

$$r = (k_1 + k_2)[H_2O_2]^{\alpha}[S_2O_3^{2-}]^{\beta}$$

The reaction between thisulphate and hydrogen peroxide is:

$$2S_2O_3^{2-} + 8H_2O_2 \rightarrow 6H_2O + 4SO_4^{2-} + 4H^+$$

From the stoichiometry, 2 mol $S_2O_3^{2-}$ will produce 4 mol of SO_4^{2-}. Thus, 1 g of SO_4^{2-} will be produced from 0.583 g $S_2O_3^{2-}$ (MW of $S_2O_3^{2-}$ = 112g/mol, MW of SO_4^{2-} = 96g/mol)

0.583 will be multiplied with the sulphate concentration to give the thiosulphate consumed. The value will be deducted from the initial concentration/2 to give the unreacted thiosulphate

Table 4.4: Unreacted thiosulfate

Time (min)		0	8	16	24	32	40	48
		Unreacted thiosulfate (ppm)						
Experiment 1	400ppm	200	124.171	83.34	54.175	42.509	25.01	1.678
	600ppm	300	212.505	154.175	113.344	84.179	78.346	84.179
	800ppm	400	277.507	242.509	184.179	172.513	166.68	166.68
	1000ppm	500	360.008	319.177	272.513	260.847	255.014	231.682
	1200ppm	600	448.342	360.847	349.181	337.515	337.515	331.682
Experiment 2	0.1ppm	300	212.505	183.34	165.841	142.509	125.01	125.01
	0.2ppm	300	154.175	142.509	107.511	101.678	60.847	66.68
	0.3ppm	300	212.505	177.507	148.342	125.01	130.843	130.843
	0.4ppm	300	206.672	171.674	125.01	119.177	107.511	113.344
	0.5ppm	300	230.004	212.505	177.507	189.173	177.507	160.008

Next, graph of unreacted thiosulphate vs time for experiment 1 and 2 will be tabulate to get the data for rate modelling.

Experiment 1:

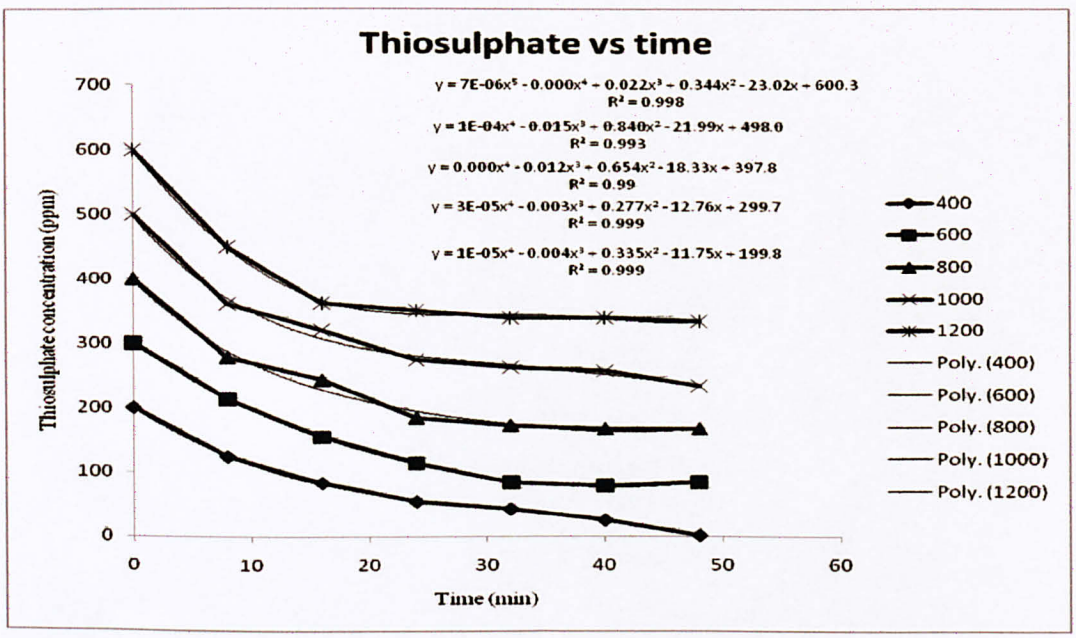


Figure 4.4: Thiosulfate concentration vs time (experiment 1)

Table 4.5: Data for rate law (experiment 1)

ppm	200	300	400	500	600
mol/L	0.001786	0.002679	0.003571	0.004464	0.005357
rate	11.75	12.76	18.33	21.99	23.02
ln S_2O_3	-6.32794	-5.92247	-5.63479	-5.41165	-5.22932
ln r	2.463853	2.546315	2.908539	3.090588	3.136363

Next, a graph of ln S_2O_3 vs ln r will be tabulate to get the value of β

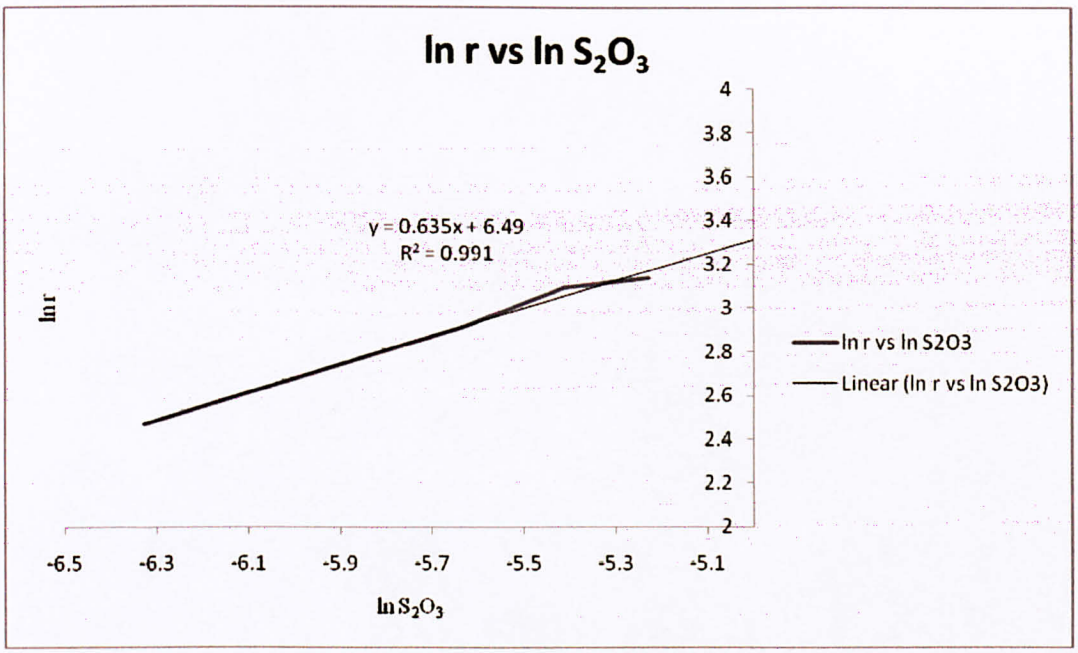


Figure 4.5: Graph of ln r vs ln thiosulfate

The value of β is 0.635, k_2 = 658.52

Experiment 2:

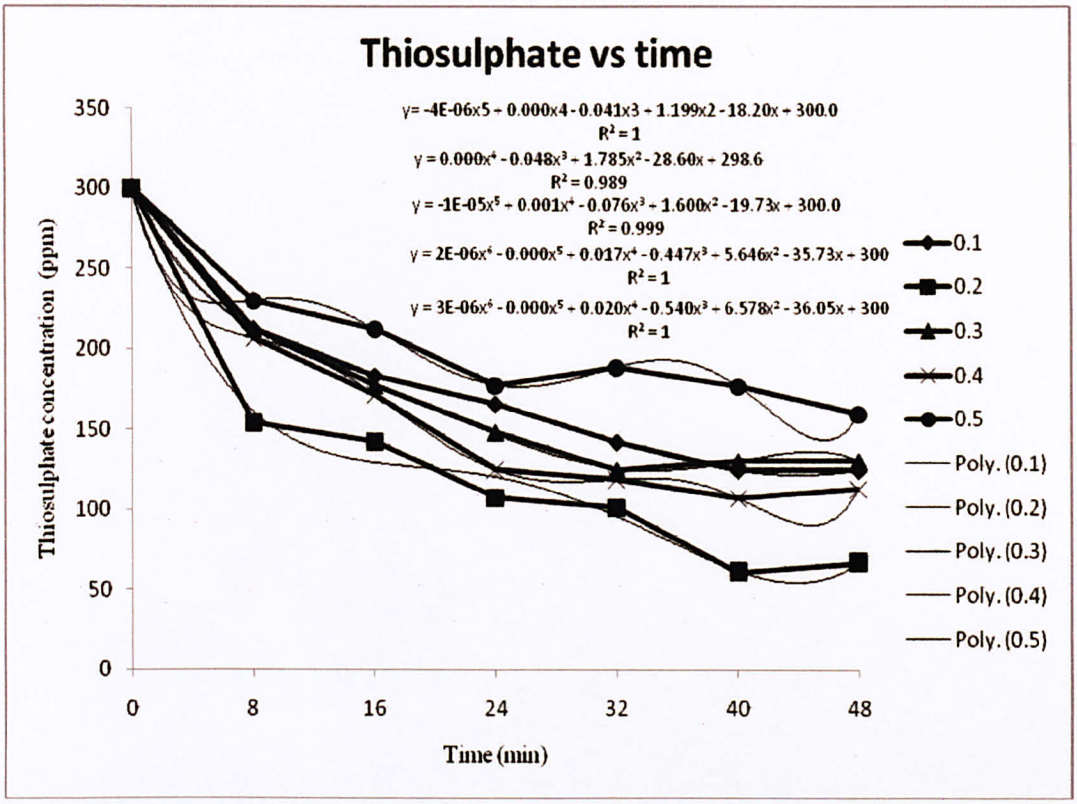


Figure 4.6: Thiosulfate concentration vs time (experiment 2)

Table 4.6: Data for rate law (experiment 2)

mol H_2O_2	0.1	0.2	0.3	0.4	0.5
rate	18.2	28.6	19.73	35.73	36.05
ln H_2O_2	-2.30259	-1.60944	-1.20397	-0.91629	-0.69315
ln r	2.901422	3.353407	2.98214	3.575991	3.584907

Next, a graph of ln H_2O_2 vs ln r will be tabulate to get the value of α

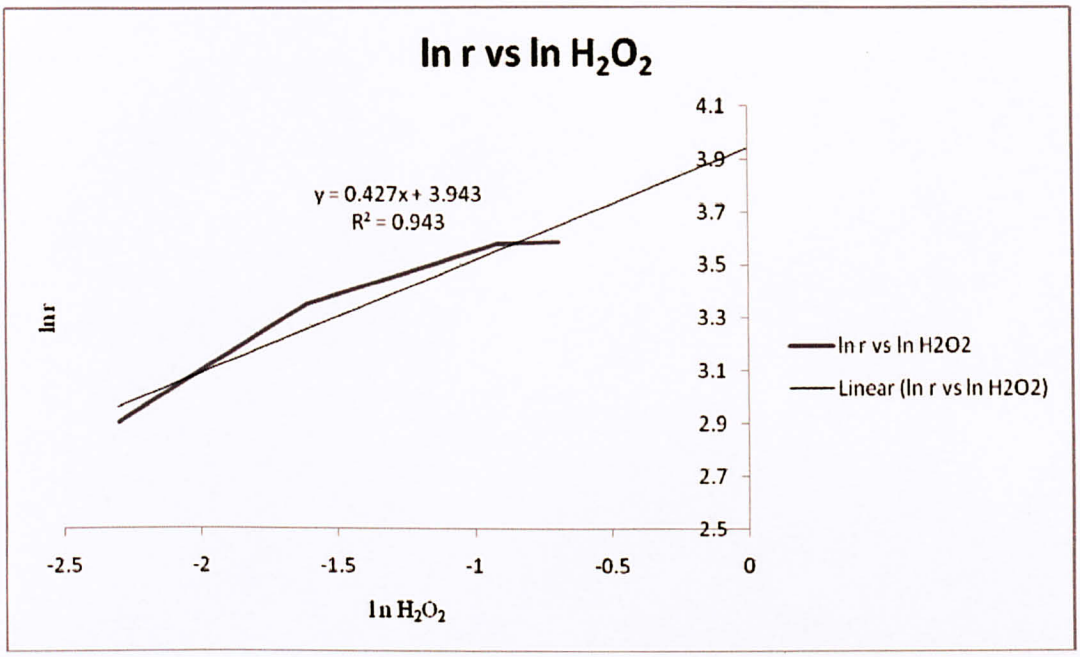


Figure 4.7: Graph of ln r vs ln hydrogen peroxide

The value of α is 0.427, $k_1 = 51.57$

Lastly, the value of α, β, k_1 and k_2 obtained will be substituted into rate equation to give $r = 710.09 \left[H_2O_2\right]^{0.427} \left[S_2O_3^{2-}\right]^{0.635}$

CHAPTER 5

CONCLUSION AND RECOMMENDATION

1. CONCLUSION

i) UV/H_2O_2 AOP is proven efficient for thiosulfate removal and the presence of UV light do helps to increase the removal rate.

ii) The rate law is dependent on both thiosulfate and hydrogen peroxide concentration but more dependent on thiosulfate concentration since β value is higher as compared to α.

iii) The optimum dosage for hydrogen peroxide is 0.2M and UV power of 12W

2. RECOMMENDATION

i) To test for different oxidizing agent besides hydrogen peroxide

ii) To test for different AOP method i.e Fenton process, ultrasonic etc.

iii) To test for higher power supply of UV light

iv) To test for more value of constant variable instead of 600ppm thiosulfate,4W UV, and 0.1M hydrogen peroxide.

v) To test for the temperature effect to the reaction.

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